- coronarium Koenig and Etlingera cevuga Smith, J. Essent. Oil Res., 5, 55-59 (1993).
- I. Vahirua-Lechat, Contribution à l'étude des composés organiques volatils d'huiles essentielles de plantes aromatiques médicinales polynésiennes, Thèse de Doctorat, (Université de Montpellier II), Montpellier, France (1994).
- I. Vahirua-Lechat, C. Menut, G. Larnaty and J-M. Bessière, Huiles Essentielles de Zingibéracées de Polynésie-Française, (Numéro spécial) Rivista Ital. EPPOS, 627-638 (1996).
- E. Von Sidow, K. Anjou and G. Karlsson, Arch. of Mass Spectral Data, 1, 392 (1970).
- R.P. Adams, Identification of Essential Olls by Ion Trap Mass Spectrometry, Academic Press, New York, NY, (2001).
- N.W. Device, Gas chromatographic retention indices of monoterpenes and sesquiterpenes on methyl silicone and Carbowax 20M phases. J. Chromatogr., 503, 1-24 (1990).
- W. Jennings and T. Shibamoto, Qualitative analysis of Flavor and Fragrance Volatiles by Glass Capillary Gas Chromatography, Academic Press, New York (1980).
- D. Joulain and W. A. König, The Atlas of Spectral Data of Sesquiterpene Hydrocarbons, E. B. Verlag, Hamburg, Germany (1998).

The Essential Oil of the Genus *Brachanthemum* from Mongolia

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Abstract

The essential oil of the leaves of Brachanthemum gobicum Krasch., B. mongolicum Krasch. and B. mongolorum Grub. were investigated by GC and GC/MS. The clear essential oil of B. gobicum was dominated by 1,8-cineole (42.6%) and camphor (29.1%) with moderate amounts of camphene (6.1%), α-pinene (2.5%), p-cymene (1.8%), terpinen-4-ol (1.8%) and cis-sabinene hydrate (1.3%). The oil of B. mongolicum had an abundance of camphor (39.5%) and 1,8-cineole (20.2%) and with moderate amounts of camphene (11.5%), borneol (9.5%), bornyl acetate (4.1%), cis-thujone (1.9%), α-pinene (1.3%) and p-cymene (1.1%). The major constituents of the blue oil of B. mongolorum were chamazulene (18.3%) and 1,8-cineole (14.6%) followed by (β)-caryophyllene (7.2%), germacrene D (5.4%), dehydro-1,8-cineole (4.5%), p-cymene (3.8%), (E)-β-ocimene (3.6%), caryophyllene oxide (2.7%) and limonene (2.3%).

Key Word Index

Brachanthemum gobicum., Brachanthemum mongolicum., Brachanthemum mongolorum., Asteraceae, essential oil composition, camphor, chamazulene, 1,8-cineole.

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Introduction

Brachanthemum is a scarcely studied genus with ten central Asian and Chinese species according to Mabberley (1). In Mongolia, the genus Brachanthemum Krasch. is represented by three species: B. gobicum Krasch., B. mongolicum Krasch., and B. mongolorum Grub (2). The essential oils of the genus have not received much attention. Shatar (3.4) made an oral report on the oil of B. gobicum along with related species and in their investigation reported quaiol (12.4-31.6%), camphor (5.6%) and terpinen-4-ol as major constituents of the resin oil from the stems of Brachanthemum gobicum from Mongolian Gobi. Shatar and Adams (5) analyzed the blue oil of B. mongolorum and reported 13.2% chamazulene, plus large amounts of 1,8-cineole (14.7%) and camphor (8.5%), with moderate amounts of germacrene D (6.3%), β-caryophyllene (6.2%), borneol (4.3%), myrcene (3.8%), (E)- β -ocimene (2.8%), p-cymene (2.7%), caryophyllene oxide (2.5%) and limonene (2.0%). However, the analysis was based on total ion counts (TIC) on a Finnigan Ion Trap machine (5). No analysis of the essential oil of B. mongolicum was found in the open literature.

Khanina et al (6) identified 47 components in the oil of B. baranovii (Krasch ex Poljak) Krasch. from Russia's Central Altair mountains. Tsevelev (7) reported the major components of B.baranovii as 1.8-cineole (23.9%), camphor (17.3%), terpinen-4-ol (13.6%), γ -terpinene (5.4%) and α -terpineol (2.6%).

The purpose of this paper is to compare the essential oils of all three of the Mongolian *Brachanthemum* species utilizing analyses on an HP MSD spectrometer with quantitation by FID.

Experimental

Plant material: Plant material was collected from native plants of B. gobicum in the middle Gobi-Tsagaan Suvraga, Adams/Shatar 7524, 7525, 7605; B. mongolicum in the Dzungarin Gobi in the Baitag Bogd-Ula mountains, Adams/Shatar 7606; and B. mongolorum in the Tsog Undur-Ula mountains of eastern Mongolia, Adams/Shatar 7521, 7522, 7523. Voucher specimens have been deposited at the herbarium of the Institute of Botany of the Mongolian Academy of Science. Ulaanbaatar-51, Mongolia.

Isolation of oils: Air dried leaves (200 g) were water-distilled for 2 h using a circulatory Clevenger-type apparatus (8). The oil samples were concentrated (diethyl ether trap removed) with N₂ and the samples stored at -20°C until analyzed. The exhausted leaves were oven dried (48 h at 100°C) for determination of oil yields (0.32–0.6 mL).

Analyses: Oils from each of the taxa were analyzed and average values were reported. The oils were analyzed on a HP5971 MSD mass spectrometer, scan time 1 sec., directly coupled to a HP5890 gas chromatograph, using a J&W DB-5, 0.26 mm x 30 m, 0.25 micron coating thickness, fused silica capillary column. The column was programmed from 60–240°C at 3°C/min. Identifications were made by library searches of the authors' volatile oil library (9), using the HP Chemstation library search routines, coupled with retention time data of

authentic reference compounds. Quantitation was by FID on an HP 5890 gas chromatograph using a J&W DB-5, 0.26 mm x 30 m, 0.25 micron coating thickness, fused silica capillary column, programmed under the same conditions as above using the HP Chemstation software,

Results and Discussion

The clear essential oil of B. gobicum (from two sites in the Gobi desert) was dominated by 1,8-cineole (39.1%, 42.6%) and camphor (27.4%, 29.1%) with moderate amounts of camphene (3.4%, 6.1%), \alpha-pinene (1.4%, 2.5%), p-cymene (3.4%, 1.8%), terpinen-4-ol (2.5%, 1.8%) and cis-sabinene hydrate (0.5%, 1.3%). The oil of B. mongolicum was clear and similar to B. gobicum in having an abundance of camphor (39.5%) and 1,8-cineole (20.2%) and moderate amounts of camphene (11.5%), \alpha-pinene (1.3%) and p-cymene (1.1%). However, the B. mongolicum oil differed from B. gobicum in having moderate amounts of borneol (9.5%), bornyl acetate (4.1%), α -thujone (1.9%) and β -thujone (0.5%) and cischrysanthenyl acetate (0.5%). The major constituent of the blue oil of B. mongolorum was chamazulene (18.3%) giving the oil its bright blue color. The second major constituent of the oil was 1,8-cineole (14.6%) followed by β -caryophyllene (7.2%), germacrene D (5.4%), dehydro-1,8-cineole (4.5%), p-cymene (3.8%), (E)-β-ocimene (3.6%), caryophyllene oxide (2.7%) and limonene (2.3%). It is noticeable that the oil of B. mongolorum was rich in many minor sesquiterpenes not found in either B. gobicum or B. mongolicum. All results can be seen in Table I.

This report utilizing FID data for B. mongolorum is similar to the previous report (3) based on Ion Trap TIC (ITTIC) data. For example, comparing FID vs. ITTIC (from 3): chamazulene (18.3%, 13.2%), 1,8-cineole (14.7%, 14.7%), camphor (10.0%, 8.5%), β -caryophyllene (7.2%, 6.2%), germacrene D (5.4%, 6.3%) and caryophyllene oxide (2.7%, 2.5%). However, this is not always the case for FID and ITTIC data.

These data from essential oils support a close relationship between B. gobicum and B. mongolicum with B. mongolorum being about equally separated from the other two taxa.

References

- D.J. Mabberley, The plant book, 2nd Ed. Cambridge UP, Cambridge, UK (2007).
- V.I.Grubov. Key to the vascular plants of Mongolia. Nauka Leningrad. Russia. (1982)
- S. Shatar, Chemistry of terpene hydrocarbons of some endemic essential oil plants of Mongolia. Symp. Pap. 11th IUPAC Intl. Symp. Chem. Nat. Prod. Vol 2. 461-462 (1978).
- S.Shatar. Chemical investigation of Essential oil from Mongolian flora. pp 90-91, Nauka Ulaanbaatar. Mongolia (1998).
- S. Shatar and R.P. Adams, The essential oil of Brachanthernum mongolorum Grub. from Mongolian paleo-endemic plant. J. Essent. Oil-Bear, Plants 4, 1-4 (2001).
- M.A. Khanina, E.A. Serykh, A.I. Pyak, L.M. Pokrovskii and A.V. Tkachev. The essential oil of Relic species Brachanthemun baranovii Krasch. J.Chem. Raw Veg. 3, 57-62 (1999).
- N.N. Tsvelev. The flora of USSR. Vol XXVI. 390-397. Publishing House of Academy of the Science of USSR. Moscow-Leningrad (1961).

Table I. Composition of the leaf oils of Brachanthemum gobicum, B. mongolicum and B. mongolorum from Mongolia

RI	Compound	B.go	bicum	B.mongolicum	B.mongolorum	B.Baranovii [6,7
846	(E)-2-hexenal		0.2	0.1	t	· •
906	santolinatriene	-	-	0.1	•	•
921	tricyclene	0.2	0.3	0.6	t .	t
924	α-thujene	0.4	0.3	0.1	0.2	0.1
32	α-pinene	1.4	2.5	1.3	0.6	0.2
946	camphene	3.4	6.1	11.5	1.3	. 0.7
959	heptanol .	-	-	0.1	-	•
960	isoamyl propionate	-	-	0.3	-	-
969	sabinene .	0.3	1.0	0.3	0.9	0.9
974	1-octen-3-ol	•	-	•	t	0.1
974	β-pinene	0.7	1.2	0.8	0.7	0.2
981	6-methyl-5-hepten-2-one	-	-	t	-	-
988	myrcene	-		0.4	4.5	•
988	dehydro-1,8-cineole	0.6	0.7	-	-	0.5
002	α-phellandrene	t	0.1	•	0.1	
007	isoamyl isobutyrate	•	0.2	0.2	-	•
011	2,3,4-trimethyl pentane*	-	0.7	0.3	•	•
014	α-terpinene	0.7	0.8	t	0.3	2.8
020	p-cymene	3.4	1.8	1.1	3.8	1.6
024	limonene	-	-	-	2.3	•
026	1,8-cineole	39.1	42.6	20.2	14.6	23.9
032	(Z)-β-ocimene	•	-	•	0.7	-
044	(E)-β-ocimene		-	-	3.6	•
049	amyl isobutyrate	-	-	t	-	
052	isoamyl butyrate		-	t	-	•
054	γ-terpinene	0.4	1.2	0.4	1.7	5.4
065	cis-sabinene hydrate	0.5 -	1.3	0.2	1.1	0.5
080	artemisia alcohol	•	t	t	•	•
086	terpinolene	-	0.3		0.2	1.3
095	linalool	0.1	-	•	0.8	0.4
098	trans-sabinene hydrate	0.2	1.0	0.2	0.8	-
100	isoamyl 2-methylbutyrate	-	0.2	0.2		-
100	2-methylbutyl 2-methylbutyrate	0.7	0.2	0.2	•	•
100	n-nonanal	0.7	0.0		- 0.4	•
101	α-thujone (=cis-thujone)	- t	-	- 1.9	0.4	•
103	2-methylbutyl isovalerate		0.1	1.9 t	-	-
1112	β-thujone (= <i>trans</i> -thujone)	0.9	-	0.5	-	•
1118	cis-p-menth-2-en-1-ol	t t	0.4		-	•
122	α-campholenal		0.4	, 0.1 0.1	-	•
124	chrysanthenone		-	0.1	-	0.2
127	aromatic terpene, FW 150, 41,69,81,135	-	•	0.7	•	0.2
1141	•	07.4	20.1		-	17.0
160	camphor pinocarvone	27.4 -	29.1 0.4	39.5 0.5	10.0	17.3
165	•					•
	borneol	0.4	0.8	9.5	4.8	-
174	terpinen-4-ol	2.5	1.8	0.6	1.4	13.6
179	p-cymen-8-ol	8.0	t	•	•	•
186	α-terpineol	2.7	1.4	0.2	1.8	2.6
194	myrtenol	0.2	0.1	0.1 ′	•	0.2
195	cis-piperitol	0.1	0.1	-	-	0.3
227	cis-p-mentha-1(7),8-dien-2-ol	-	0.1	•	•	•
234	ascaridole	-	0.1	-	•	0.1
235	neral	•	-	•	-	
261	cis-chrysanthenyl acetate	0.2	-	0.5	•	-
264	geranial	-	-	-	0.1	-
284	bornyl acetate	-	- \		-	0.1
288	lavandulyl acetate	-	-	0.4	-	. •
299	terpinen-4-yl acetate	•	0.1	0.2	-	. 0.2
316	δ-terpinyl acetate	1.3	0.1	t "	-	•
1346	α-terpinyl acetate	0.2	0.6	0.5	-	1.1
1373	α-ylangene .	-	-	-	0.3	-
1374	α-copaene	0.1	0.1	- ·	. -	0.3
1379	geranyl acetate		-	t		-
1383	isobornyl propionate	-	-	* t	•	•
1387	β-bourbonene	-	-	-	0.5	-

Table I. Continued

Table I. Softunded									
RI .	Compound β-caryophyllene	B.gobicum		B.mongolicum	B.mongolorum	B.Baranovii [6,7]			
1417		0.2	•	•	· 7.2	0.2			
1452	α-humulene	-	-	-	0.5	0.1			
1454	(E)-β-farnesene	-	-	-	0.4	•			
1481	γ-curcumene		-	•	1.2	-			
1484	. germacrene D	-	0.2	. •	5.4	2.4			
1489	β-selinene	-	0.3	•	1.0	•			
1493	zingiberene	-	-	•	0.9	•			
1500	bicyclogermacrene	-	-	-	0.7	1.1			
1508	germacrene A	-	-	-	0.2	•			
1521	β-sesquisphellandrene	-	-	•	0.3	•			
1577	spathulenol	· 1.2	-	-	1.0	1.5			
1582	caryophyllene oxide	• •	-	-	2.7	•			
1587	davanone	0.2	0.2	-	-	•			
1607	(Z)-sesquilavandulol	-		•	0.4	•			
1674	α-bisabolol	•	-	•	0.3	•			
1685	germacra-4(15),5,10(14)-trien-1-al		-		0.5	. · · · ·			
1730	chamazulene	-	-	-	18.3	•			
1983	5,6-dihydrochrysene*	-	-	•	0.2	•			
2100	heneicosane	_	-	-	0.3	-			
2300	tricosane	•	-	•	0.6	•			

s Gobi = south side of Gobi desert, m Gobi = middle region of Gobi desert. RI = Arithmetic Index on DB-5(= SE54) column. 'Tentatively identified. Compositional values less than 0.1% are denoted as traces (t). Unidentified components less than 0.5% are not reported. Those compounds that appear to distinguish taxa are in boldface.

R. P. Adams, Cedar wood oil: analysis and properties. In Modern Methods of Plant Analysis: Oils and Waxes. Edits., H.F. Linskins and J.F. Jackson, pp. 159–173, Springler-Verlag, Berlin, Germany (1991).

R. P. Adams, Identification of Essential Oils Components by Gas Chromatography/Mass Spectrometry, Allured Publ. Corp., Carol Stream, IL, (2006).